

Hexazinone Residues in Surface and Groundwater at Two Sites Within Agassiz Provincial Forest, Manitoba, Canada



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D. A. Williamson
Environment Officer
Water Standards and Studies
Department of Environment and
Workplace Safety and Health

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Abstract

Studies were undertaken at two sites within Agassiz Provincial Forest, Manitoba, Canada, to determine the fate and effect of Velpar L on aquatic systems. Velpar L contains the active ingredient hexazinone in a 240 g/L water dispersible solution and was used to control deciduous vegetation in reforestation plantations. Surface water and groundwater were monitored for hexazinone residues. Conventional flask and microplate algal bioassays were conducted using the unicellular alga Selenastrum capricornutum Printz and a Microtox bioassay was undertaken using Photobacterium phosphoreum. Such bioassays were conducted to assist in inferring the nature and extent of potential impacts of hexazinone on surface water systems.

Both lateral off-site migration and vertical migration of hexazinone were observed within the surficial aquifer at the study sites. Lateral movement was limited to the extent that less than 10 µg/L were detected in groundwater samples within 5 m of the application site. Hexazinone residues were detected in test wells for a period of approximately 1000 days following application. Hexazinone appeared to move downward in a relatively narrow band at a rate that was artificially enhanced due to the effect of groundwater sample extraction. The maximum observed hexazinone concentration in groundwater was less than 2.0% of the calculated tentative maximum acceptable drinking water criteria derived for the protection of human health. Velpar L was not mutagenic as evidenced by a S.O.S. chromotest using the bacterium Escherichia coli.

Hexazinone residues were detected within ephemeral pools that formed on treated soils for a period of approximately 1000 days following application. It was determined that the principal impact upon surface water aquatic systems following hexazinone contamination, would result from inhibition of primary productivity. Such impacts would be realized at relatively low hexazinone concentrations (22.5 µg/L) as determined by algal bioassay studies. Secondary effects may then be manifested in other ecological compartments, depending upon the magnitude and duration of contamination.

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1.0 Introduction

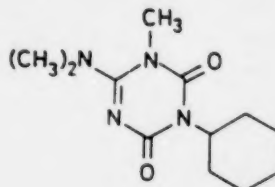
Integral to the judicious management of Manitoba's forestry resources is the replenishment of harvested natural stocks through silviculture management techniques. Endorsement of the Canada-Manitoba Forestry Renewal Agreement has provided long-term commitment and direction to such activities. Forestry management professionals in Manitoba have recently recognized the value of herbicides as a tool for the enhancement of growth within reforestation plantations. Properly utilized herbicides can reduce the human and financial resources required for initial plantation site preparation and can improve the yield potential of coniferous species through reducing the competition from herbaceous weed growth and from deciduous shrubs and trees.

While herbicide use within the agricultural industry is well established, such use within the forestry industry is still in its infancy, at least in Manitoba. Consequently, many questions regarding herbicide transport, fate and effect within the environment unique to Manitoba's forests must be resolved before widespread use prevails.

Velpar L has been used for the past several years by the Forestry Branch, Eastern Region, Manitoba Department of Natural Resources, within Agassiz Provincial Forest, for conifer release on several reforestation plantations.

Velpar L, is manufactured by E.I. du Pont de Nemours and Company (Inc.), Wilmington, Delaware. It is temporarily registered in Canada for application in forestry management (Reg. No. 18197, Pest Control Products Act). Velpar L contains the active ingredient hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1, 3,5-triazine-2,4 (1H, 3H)-dione) in a water dispersible solution

(240 g/L). Hexazinone has a molecular formula of $C_{12}H_{20}N_4O_2$ and a molecular weight of 252.3. The structural formula is as follows (Worthing and Walker 1987):



Velpar L has been used in other jurisdictions to effectively control broadleaf deciduous vegetation, such as aspen, poplar, ash, maple, birch and others in order to allow for the release of desirable coniferous species within plantation sites (Bouchard et al. 1985).

The Water Standards and Studies Section, Manitoba Department of Environment and Workplace Safety and Health undertook an environmental monitoring program at two selected sites within an area in which Velpar L had been applied. Site 83-8, 20.8 ha in area, received Velpar L by spotgun application on July 13, 16, 17 and 20, 1984 at a rate of 11.5 L/ha. Velpar L was applied to site 86-1, 13.7 ha in area, also by spotgun application, on July 25 and 26, 1985 at a rate of 12.5 L/ha.

The general objectives of the investigation were to determine if Velpar L was being leached into the groundwater or was being transported off the plantation sites by hydrological events, and if so, to determine the environmental impact of such movement. The investigation consisted of two distinct activities. Firstly, the movement of hexazinone was monitored within surface water and groundwater. Secondly, an algal bioassay was used to determine the potential of hexazinone to impact aquatic systems by inhibiting primary productivity.

2.0 Methods

2.1 Study Area

The study area is shown in Figure 1. Agassiz Provincial Forest encompasses approximately 30,000 km² and is located approximately 60 km east of Winnipeg.

The surficial geology of the study area is complex, resulting from three distinct stages of glaciation (Lebedin 1978). A schematic overview typical of the study sites is presented in Figure 2. The Belair drift, the Libau drift, and lacustrine deposition by Glacial Lake Agassiz comprised the three glaciation stages. The Belair drift was formed by the advance of a major ice sheet from the northeast. Two stratigraphic units comprise the Belair drift. Firstly, the surficial layers consist of pervious sand and gravel outwash deposits either exposed at the surface or confined between layers of silt and clay till. The outwash deposits are up to 15 m in thickness and are underlain by a granular basal layer up to 6 m in depth (Acres 1985). The Belair and Milner Ridge end moraines, which are the dominant physiographic feature surrounding the study sites, were formed by the accumulation of glacial material along the terminal front margin of this ice sheet (Lebedin 1978) or as interlobate deposits between the northeast and northwest advancing ice sheets (Teller and Fenton 1980).

The Libau drift was formed by the advance of an ice sheet from the northwest. This ice sheet over-rode the Belair drift and moved against or over the Belair and Milner Ridge end moraines. The advance and subsequent retreat of this ice sheet deposited new material and modified the morphology of the previous Belair drift (Lebedin 1978). The Libau drift consists principally of till material

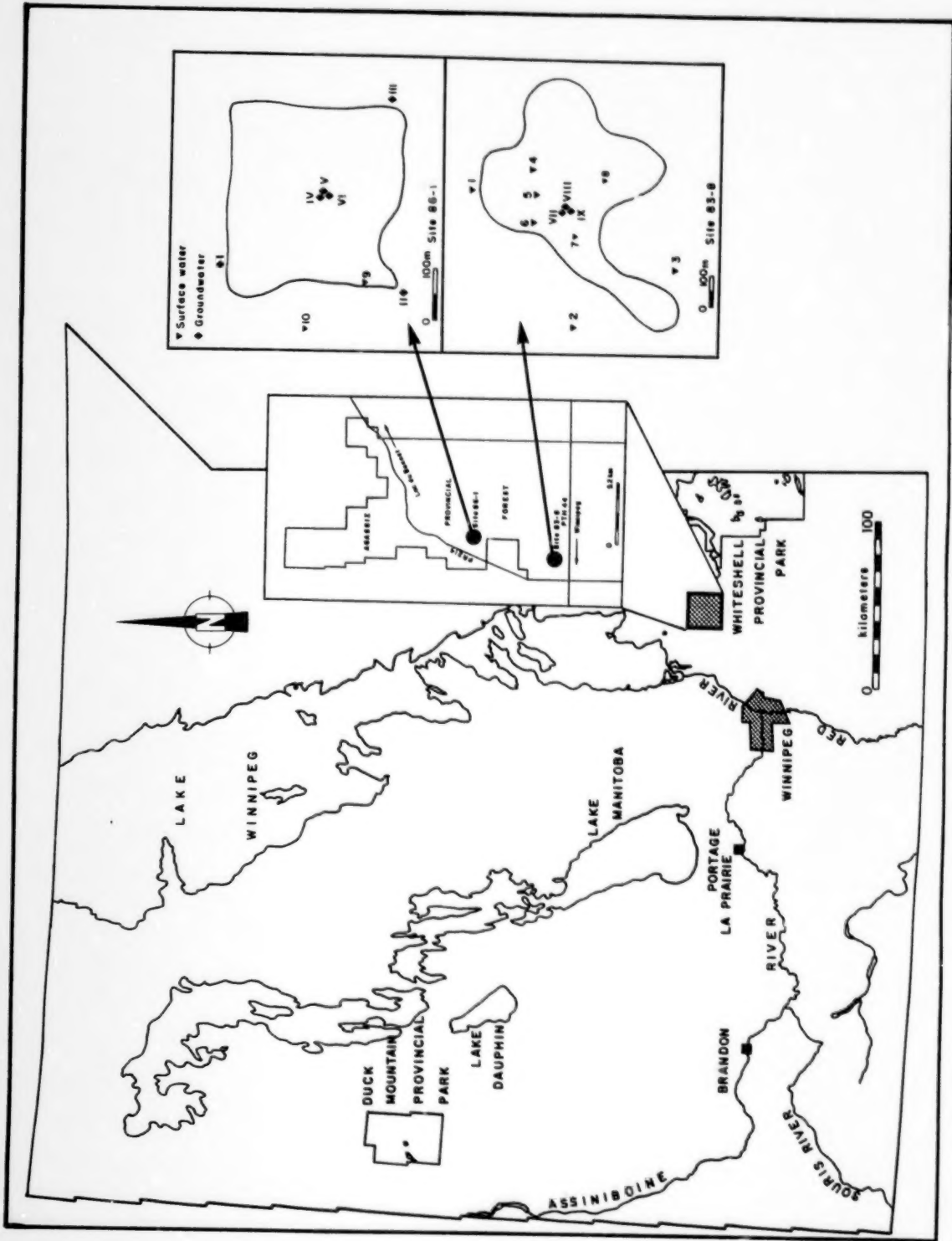


FIGURE 1: Location of study area and sampling sites.

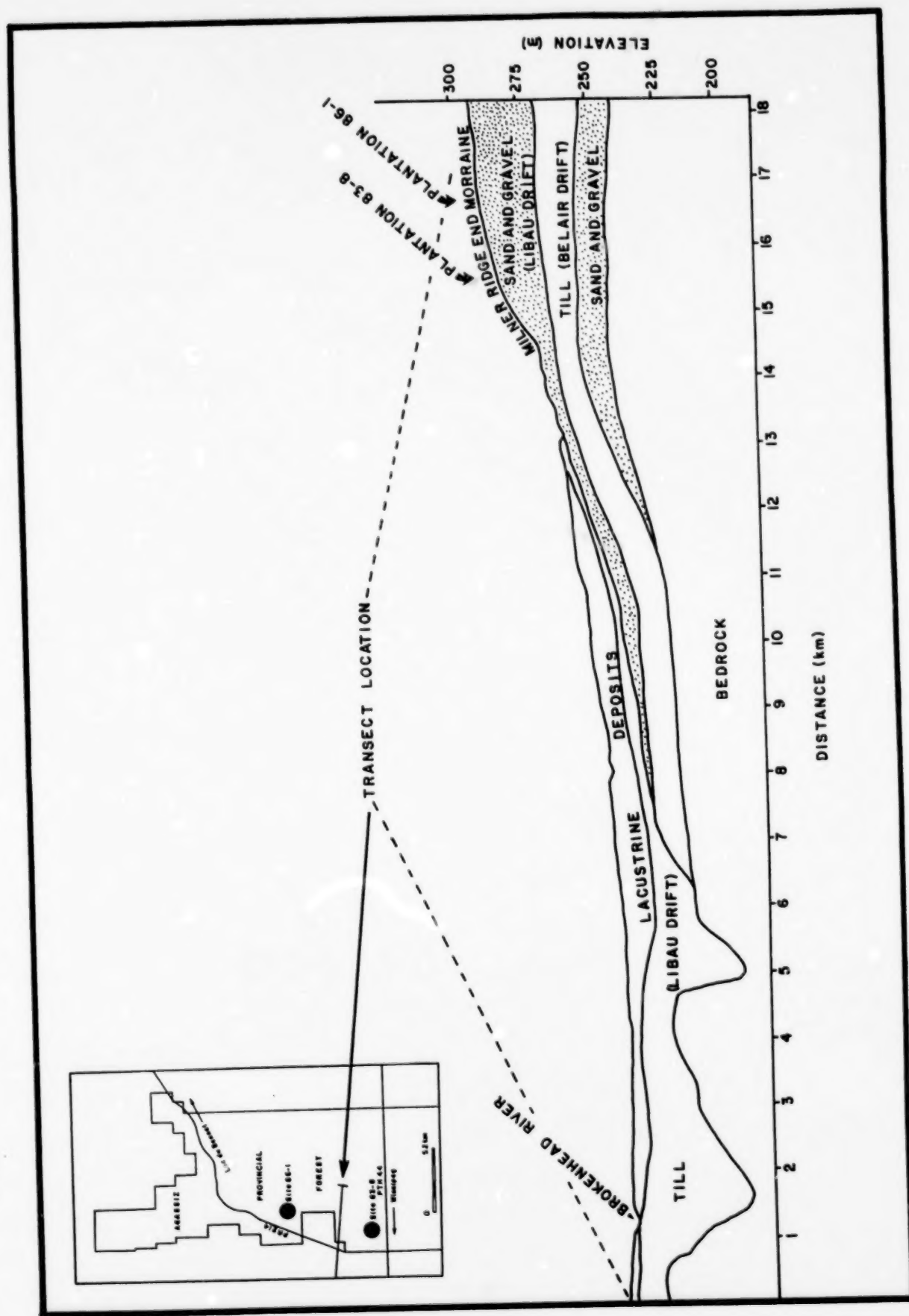


FIGURE 2: Stratigraphic overview of the study area.

and sand and gravel deposits existing as a granular cap up to 15 m in depth on the Milner Ridge end moraine. A Libau silt-clay unit also exists, and ranges up to 10 m in thickness. This silt-clay unit overlays the Belair outwash deposits (Acres 1985). Both the Belair and Libau drifts were modified into lacustrine and beach deposits by the erosional energy of Glacial Lake Agassiz (Lebedin 1978).

Two major aquifers are present within the study area. The Belair basal aquifer underlies Milner Ridge and is confined by the Belair and Libau till units and lacustrine clay deposits. This aquifer is recharged from the Milner Ridge and Belair end moraines. Artesian discharge from this aquifer occurs in several locations immediately to the west of the study area. However, the principal discharge locations are along the Brokenhead River, located 15 km to the west of the study area. The second and most important aquifer in relation to the present study is the surficial aquifer. This surficial sand and gravel aquifer is extensively exposed along Milner Ridge. Milner Ridge forms a recharge area with a high infiltration rate (Acres 1985). Discharge occurs from this surficial aquifer along the base of Milner Ridge, located immediately to the west of the study area.

Soil types within each study site are somewhat variable. Soils at plantation 83-8 are comprised of Sirko till substrate (coarse sand) and Woodridge series (sand). Natural drainage (via groundwater movement) is imperfect to excessive. The topography is comprised of gentle, irregular slopes. Native vegetation consists of aspen, birch, spruce, balsam fir and jack pine (Smith et al. 1967). Soils at

plantation 86-1 are comprised principally of sirko series (coarse sand) with soil profiles of gleyed grey wooded. Interstitial soil drainage is imperfect. The topography varies from level terrain to irregular gentle slopes. The dominant vegetation is typical of boreal forests, such as aspen, birch, balsam fir, poplar, spruce and jack pine (Smith et al. 1967).

Surface water drainage is a minor component of the hydrological cycle within the study area. Some surface water retention and groundwater discharge occurs in the numerous sphagnum peat deposits and small marshes within the region. However, most precipitation is retained within the sand and gravel deposits. Groundwater is therefore, a significant and dominant portion of the water resources within this area.

Data obtained during groundwater test well installation indicated that the surficial aquifer at plantation 83-8 extended from the ground surface to a depth greater than 18.3 m. A layer of lacustrine clay approximately 0.10 m thick was located 1.5 m below the ground surface. The substrate both above and below this clay layer consisted of sand ranging from fine silt to coarse texture. The surficial aquifer at plantation 86-1 was somewhat variable in depth and ranged from 0.8 m (well II) to 3.7 m (well I) below ground surface. Well VI was intermediate with a depth of 2.7 m. A thin layer of till was encountered at well I approximately 1.0 m below the ground surface. This till layer extended downward approximately 1.5 m. The surficial aquifer at this latter site was underlain by a layer of clay in excess of 15.24 m thick.

2.2 Surface Water Investigation

Eight sampling locations were monitored for hexazinone residues on or adjacent to plantation 83-8. Sampling sites 1, 2 and 3 were situated off-site (Figure 1). Site 1 consisted of an excavated depression approximately 1 m^3 in volume, located approximately 50 m in a northerly direction from this plantation. Site 1 was surrounded by peat deposits. Site 2, located in a fen, was similarly surrounded by peat deposits. Site 2 was located approximately 750 m in a westerly direction from plantation 83-8. Site 3 was located in a depression remaining from an abandoned gravel quarry and was situated approximately 500 m in a southerly direction from this plantation. Sampling sites 4, 5 and 8 were located in shallow depressions within treated areas of plantation 83-8. Sampling site 6 was located in a shallow abandoned well approximately 1.5 m in depth, situated in a low-lying aspen grove that extended into plantation 83-8. The area within approximately 10 m surrounding this sampling site had not received Velpar treatment. Sampling site 7 was located in an excavation approximately 2.0 m in depth. Pooled water at all sites were comprised of a combination of surficial groundwater and surface water.

Sampling site 9 was located in a low-lying area situated within Velpar treated regions of plantation 86-1. Site 10 consisted of a spring located approximately 500 m in a westerly direction from this plantation. Groundwater discharge was observed only at the time of the single sample collection.

Water samples were collected for hexazinone analyses in 1 L amber glass containers that had previously been rinsed with pesticide grade hexane and acetone. Samples were collected at variable intervals, beginning immediately prior to Velpar L application.

2.3 Groundwater Investigation

Plantations 83-8 and 86-1 were instrumented with three and six groundwater sampling wells, respectively. The wells were installed by a commercial well drilling firm (Friesen Drillers, Ltd., Dugald, Manitoba). All well casings were constructed of 2.54 cm (inside diameter) steel. Attached to these, and comprising the lower 0.914 m, were 5.08 cm (inside diameter) stainless steel screens. Silica sand was placed around the stainless steel screens in order to ensure that the screen apertures would not become entrained with fine grained parent material. Drilling fluid was obtained off-site in order to reduce the possibility of contaminating the bore holes with traces of hexazinone introduced with the drill water. The uncompacted soil horizon at plantation 86-1 dictated that bentonite mud be used to ensure that the bore holes remained open while the well casings were inserted. The bentonite was then washed to the surface by repeated flushings with drilling fluid. The surface annuli were completely sealed with concrete to prevent surface liquids from migrating down the casings to the screens and to secure the wells from possible vandalism. The casings were equipped with threaded galvanized steel caps.

Wells I and II were located approximately 5.0 m off-site plantation 86-1 in north-west and south-west directions, respectively. Well III was initially thought to be similarly located 5 m off-site plantation 86-1 in a south-east direction. However, once the herbicidal effects of Velpar L became evident on the local vegetation, it was found that this well in fact was located within 2 m of soils that had received treatment. These wells were placed at the lower portion of the first water bearing aquifer. Screened intervals extended to 4.30 m, 1.50 m and 2.85 m, respectively. Wells IV, V and VI, also located at plantation 86-1, were situated at a central location within the area treated with herbicide. These wells were placed in a common bore hole, with the stainless steel screens situated at intervals that trisected the first water bearing aquifer. The screened intervals extended to 1.35 m, 2.00 m and 3.05 m, respectively. Well VI was located at the bottom of this zone.

Wells VII, VIII and IX were located at a central area within plantation 83-8. These wells were situated within a common bore hole with screened intervals to 4.90 m, 9.30 m and 13.80 m below ground surface.

The water table at both sites 83-8 and 86-1 varied throughout the study period and ranged from approximately 0.7 m below surface during early spring to approximately 3.0 m below surface during midsummer.

The water table was measured both before and after pumping. Additionally, the piezometric surface was monitored in wells VI and

VII on several occasions while water was being pumped from well IX. This provided information regarding the pumping induced downward migration of groundwater.

The standing water within all wells was completely evacuated with the use of a gasoline operated centrifugal pump, prior to the collection of groundwater samples for hexazinone analyses. Freshly infiltrated groundwater was then collected in 1 L amber hexane/acetone rinsed sample containers with a hand operated mechanical sampler. This sampler was constructed of 1.27 cm (inside diameter) copper tubing, 93 cm in length, equipped with a steel ball foot valve. This device was rinsed with generous volumes of hexazinone-free water prior to the beginning of sampling each well. Field quality control testing indicated that hexazinone residues were not adhering to this sampler. Thus, the potential for sample cross-contamination was reduced.

2.4 Aquatic Toxicology

The toxicity of Velpar L was tested with the unicellular coccoid green alga Selenastrum capricornutum Printz. Bioassay methods were similar to Miller (1978) and Greenberg et al. (1980). Temperature was maintained at $24 \pm 2^\circ\text{C}$. Illumination was provided by "cool-white" fluorescent lighting that provided approximately 4,300 lux. Culture vessels consisted of 500 mL Erlenmeyer flasks fitted with gauze plugs. The growth medium was comprised of synthetic algal media, namely "Alga-Gro-Freshwater", purchased from Carolina Biological Supply, combined in a 4:1 dilution with deionized water. Vessels and media were sterilized by autoclaving.

Velpar L was added to each flask to reach ultimate initial concentrations of 100 µg/L, 50 µg/L, 25 µg/L, 10 µg/L and 5 µg/L. Each vessel was then inoculated with 1000 S. capricornutum Printz cells. Final culture volumes were 100 mL. Five replicates were cultured for all concentrations, including a control.

Cell reproduction was monitored with a Royco Model 927TC particle counter. The bioassay was terminated after 18 days.

The hexazinone concentration that reduced reproduction by 50% in comparison to the control was determined nomographically following probit analyses (Natrella 1966). Probit methods were also used to calculate 95% confidence limits around the median concentration (Ibid.).

Velpar L was submitted to the Environmental Protection Services Laboratory, Longueuil, Quebec for confirmatory algal bioassay and additional toxic and genotoxicity assessments. Algal microtests were performed using S. capricornutum Printz according to the methods of Blaise et al. (1986), with five replications. The principles of this method were similar to those described for the conventional flask algal bioassay. However, the specific methodology differed substantially. Most important was the use of 220 µL microplates and an abbreviated bioassay duration of 96 hours.

The toxicity of Velpar L towards bacteria was determined using 5 min. and 15 min. EC_{50} Microtox bioassays with Photobacterium phosphorium. Microtox procedures were in accordance with Beckman (1982). Fifty-percent inhibition of light in comparison to the control represented the EC_{50} end point. Genotoxicity assessment was

undertaken using the SOS inducing potency (SOSIP) procedure with the bacterium Escherichia coli. Methods were in accordance with Quillardet et al. (1982) and Organics (1986). Both the Microtox and the genotoxicity tests were conducted with three replications.

2.5 Hexazinone Analyses

Analyses for hexazinone in water was conducted in accordance with the method described by U.S. EPA (1982). A 1 L sample volume was extracted with methylene chloride using separatory funnels. The extract was dried with sodium sulphate and exchanged to hexane. The volume was concentrated to 5 mL or less. Identification and quantitation was accomplished using a gas chromatograph equipped with a nitrogen phosphorus or a Hall electrolytic conductivity detector. The limit of quantitation was usually 1.0 µg/L.

3.0 Results and Discussion

3.1 Surface Water

Hexazinone concentrations in surface water associated with plantation 83-8 are located in Table 1. Hexazinone concentration was 1.7 µg/L on one occasion at sampling site 1, located adjacent to plantation 83-8, and was less than the limit of quantitation on all other sampling occasions (Figure 3). Hexazinone was not detected at either sampling sites 2 or 3, similarly located adjacent to this plantation. The single detection off-site plantation 83-8 could have occurred for a number of reasons. These include the transfer of hexazinone with small amounts of snow melt-water runoff, field sample container contamination or analytical error, or migration with the windborne movement of leaf litter. Neary et al. (1983) determined that leaf litterfall contained up to 6.0 ppm hexazinone during the third month after application. Although leaf litter was not analyzed during the present study, this transfer mechanism nevertheless existed. The single detection indicated that the off-site migration of hexazinone via surface drainage or the movement of surficial groundwater was not significant. This is consistent with the presence of soils with good vertical interstitial water movement characteristics and the absence of well defined surface runoff channels.

Sampling sites 4, 5, 6, 7 and 8 were located within plantation 83-8 and were situated either directly on soils that had received hexazinone application or were in close proximity to such soils. Hexazinone data from these sampling sites are graphically

Table 1: Hexazinone in surface water at plantations 83-8 and 86-1.
Concentrations are reported in µg/L.

	83-8										86-1	
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10		
July 3, 1984	^a	<0.30	<0.30									
July 26, 1984		<0.30	<0.30									
August 30, 1984	^b	<3.0 ^b	<0.30									
October 9, 1984	<0.30	<0.30	<0.30									
April 24, 1985	<1.0	<1.0	<1.0									
May 13, 1985	<1.0	<1.0	<1.0	80.0								
June 4, 1985	<1.0	<1.0	<1.0	84.9	48.3	10.1						
July 16, 1985	<1.0	<1.0	<1.0		25.0	6.0						
August 21, 1985	<1.0	<1.0	<1.0		12.9	4.1						
September 30, 1985	<1.0	<1.0	<1.0		14.0	17.5						
October 22, 1985	<1.0	<1.0	<1.0		<5.0 ^c	<5.0 ^c						
May 13, 1986	1.7	<1.0	<1.0	6.9	8.4	2.2	7.9		71.6	<1.0		
July 14, 1986	<1.0	<1.0	<1.0		6.8	4.0						
August 6, 1986	<1.0	<1.0	<1.0			1.9		27.8				
May 12, 1987	<1.0	<1.0	<1.0	1.5	4.2	1.6	7.4					
July 21, 1987	<1.0		<1.0			<1.0						
October 1, 1987	<1.0		<1.0			<1.0						

^a Sample contamination occurred as a result of transporting and handling Velpar L.

^b Lack of sufficient sample volume - detection limit increased.

^c Unknown interference - detection limit increased.

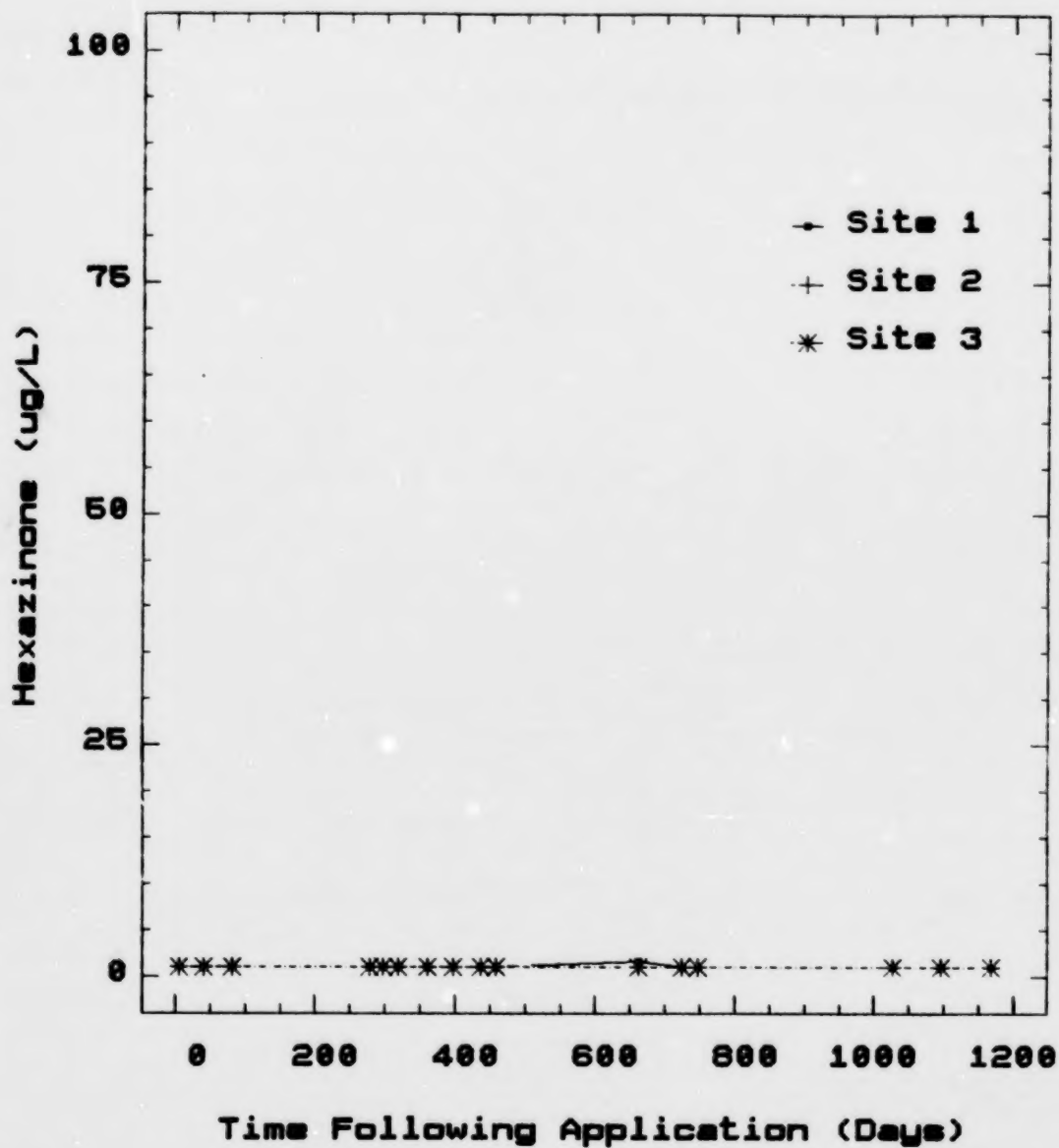


Figure 3: Hexazinone residues in surface water adjacent to plantation 83-8.

represented in Figure 4. Maximum concentrations of hexazinone were detected at most sites during the first sampling period that coincided with the presence of intermittently pooled water. Such samples were collected approximately 300 days after hexazinone treatment. Concentrations diminished to near or below the analytical limit of quantitation. Hexazinone residues persisted within treated soils or were recycled through litterfall such that leaching into surface water and surficial groundwater occurred for more than 1000 days following treatment.

Sampling sites 9 and 10 were located within or near 86-1. Topography and soils generally precluded the pooling of surface water within the treated area. However, one sample was collected during the early spring, 1986. The concentration of hexazinone was similar to concentrations observed at plantation 83-8. One additional sample was collected during this period from a spring, located approximately 500 m downgradient from plantation 86-1. Hexazinone residues were not detected at this location.

Hexazinone residue analysis within the surface 50 cm soil profile was conducted at plantation 83-8 immediately following treatment and was repeated approximately 90 and 300 days later (Phillips pers. com.). The data indicated that hexazinone residues within the surface soils immediately following treatment ranged from

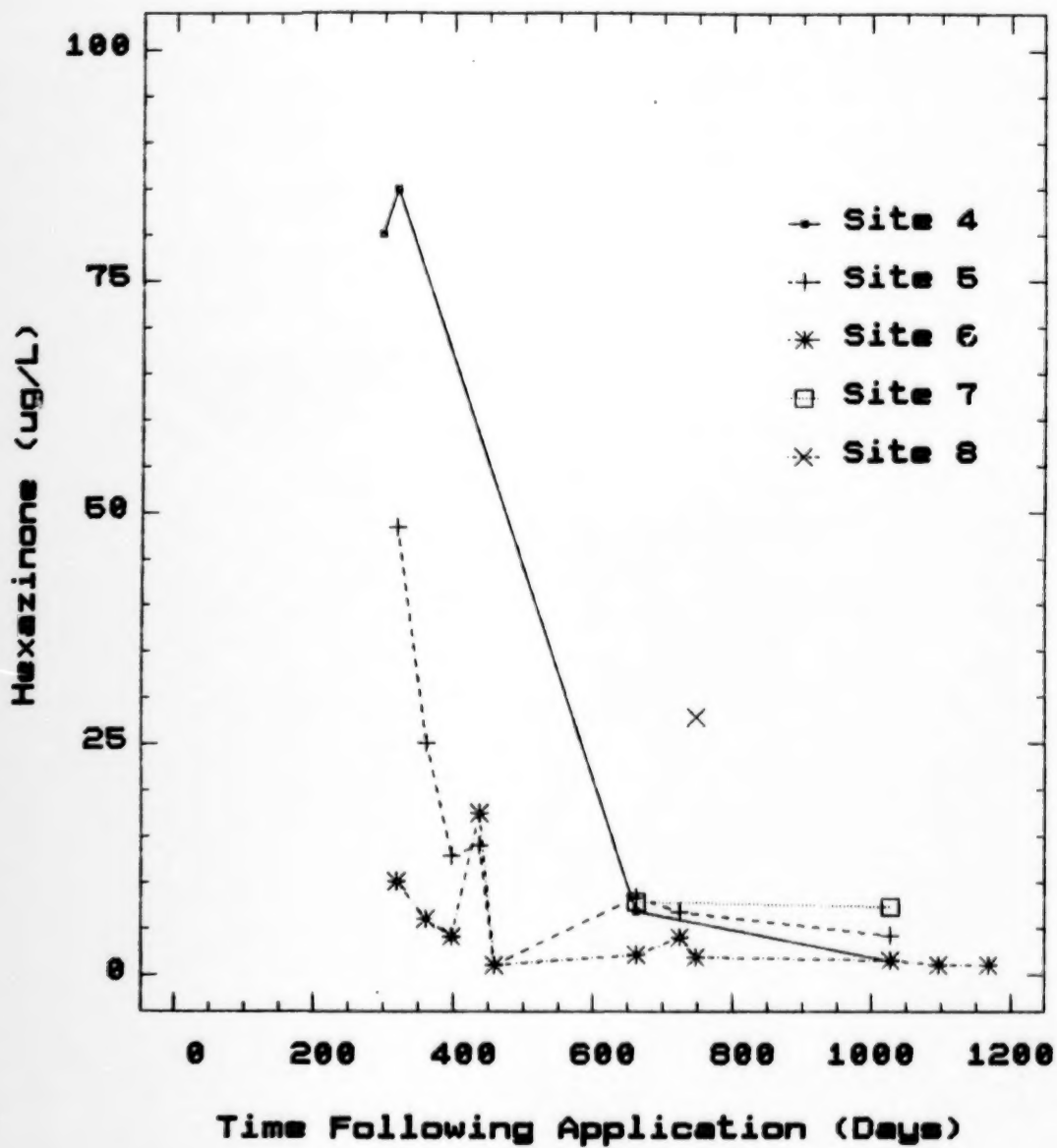


Figure 4: Hexazinone residues in surface water within plantation 83-8.

3257.8 $\mu\text{g}/\text{cm}^2$ to 4952.7 $\mu\text{g}/\text{cm}^2$. These initial surface soil concentrations were then reduced to approximately 60 $\mu\text{g}/\text{cm}^2$ during the following 90 days. Hexazinone residues were present at trace concentrations at the 10 cm, 30 cm, and 50 cm depths 90 days after treatment. Such data indicated that rapid downward migration past the 50 cm depth probably occurred during the first 90 days. Trace concentrations of hexazinone were detected within the surface soils approximately 300 days following treatment, although data were somewhat variable between sample replicates. Hence, hexazinone was available for leaching into surface water and surficial groundwater pools during this period.

Feng (1987) examined the movement of hexazinone in silt-loam soils in the Peace River region of British Columbia for 104 days following application. It was determined that vertical leaching of hexazinone did not occur beyond 15 cm. Hexazinone was not detected 20 m and 40 m adjacent and downslope (5 to 10% gradient) to the application site. Analyses of metabolites indicated that degradation occurred principally by hydroxylation and that demethylation activity was low.

The half-life of hexazinone in soils is reported to range from 1 to 12 months depending upon local climatic conditions and soil types (Ghassemi et al. 1982). However, most studies have been conducted under conditions unique to the southern United States and may not be directly comparable to Manitoba's continental sub-arctic climate. Ghassemi et al. (1982) further reported that degradation in soil is due to microbial action under both anaerobic and aerobic

conditions, although the rate is slightly reduced under anaerobic conditions. Volatilization from soil surfaces was negligible due to its low vapor pressure (Ibid.). Hexazinone in surface soils, however, is subject to degradation by photolysis. Similar degradation pathways have also been reported for hexazinone in water (Ibid.).

Data from the present study are not suitable for the purpose of determining the half-life of hexazinone in either soils or surface water. However, the soil data indicated that the presence of hexazinone would be relatively brief, due to leaching into lower soil profiles rather than degradation.

3.2. Groundwater

Hexazinone concentrations observed within the surficial aquifer associated with plantation 83-8 are listed in Table 2 and are graphed in Figure 5. Hexazinone concentrations were initially measured at 5.5 µg/L, <1.0 µg/L, and 1.8 µg/L in wells VII, VIII, and IX, respectively. Such concentrations likely reflected slight aquifer contamination associated with the well installation. Well installation occurred approximately 400 days subsequent to hexazinone application. During the following approximately 700 days, hexazinone reached maximum concentrations first in the two most shallow wells (wells VII and VIII) then peaked at a concentration of 48.0 µg/L in the deepest well (well IX) (Figure 5). The downward movement of hexazinone in the vicinity of the wells was probably in part, artificially induced due to the extraction of water prior to and

Table 2: Hexazinone concentrations ($\mu\text{g/L}$) in groundwater at plantation sites 83-8 and 86-1.

	86-1					83-8		
	Well I	Well II	Well III	Well IV	Well V	Well VI	Well VII	Well VIII Well IX
September 30, 1985	<1.0		<1.0			27.6	5.5	3.0 1.8
October 22, 1985	<1.0		<1.0			46.2	1.4	<1.0 1.8
May 13, 1986	7.2	3.3	16.5	25.8	34.9	18.8	21.2	19.8 1.1
July 14, 1986	<1.0		20.5			12.3	21.6	10.8 48.0
August 6, 1986	5.1		18.3			12.8	4.5	3.0 7.6
May 12, 1987	<1.0	<1.0	2.4			5.2	4.2	5.3 10.2
July 21, 1987	<1.0		1.4				<1.0	<1.0 2.8
October 1, 1987	<1.0		<1.0			<1.0	<1.0	<1.0 <1.0

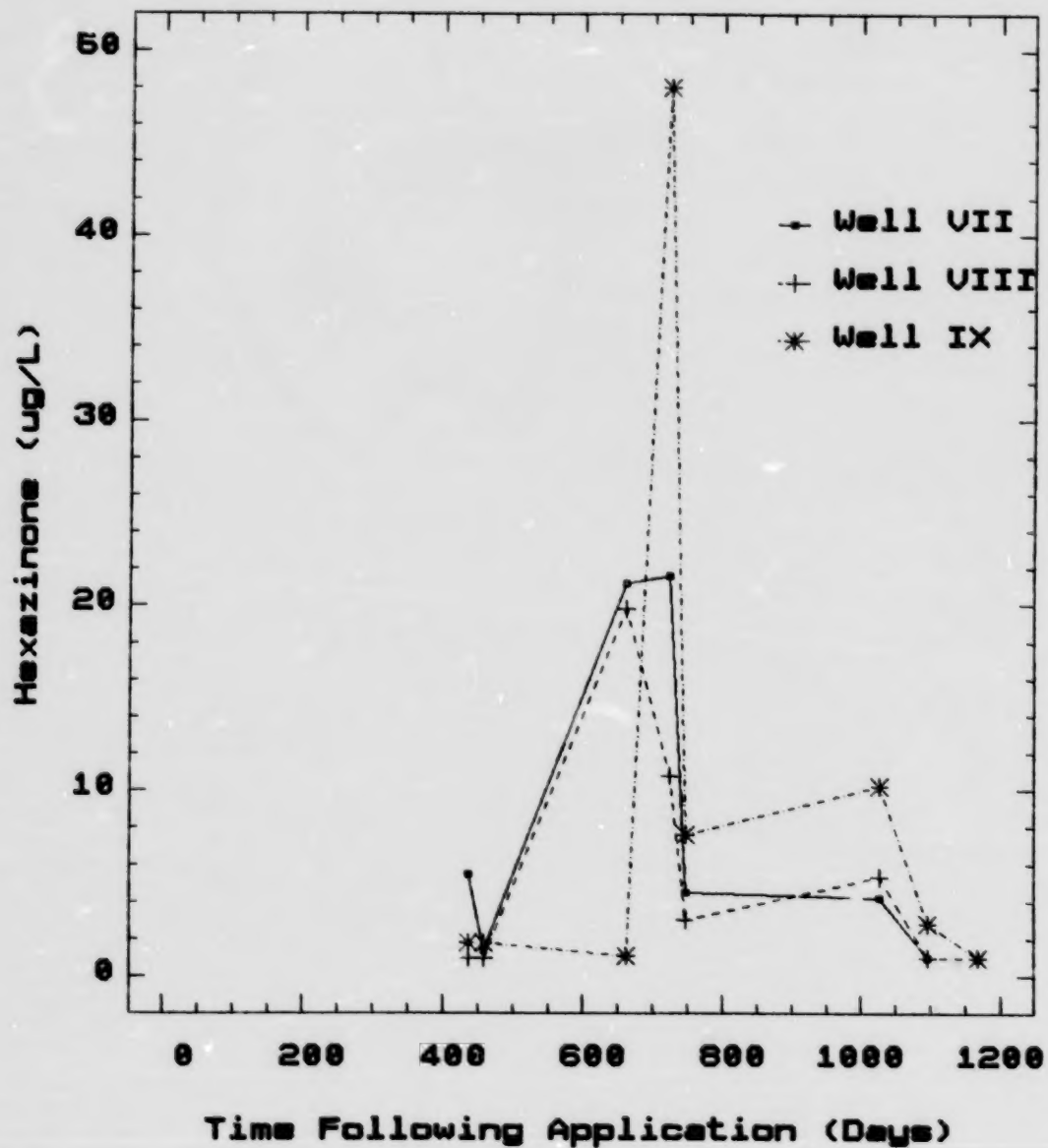


Figure 5: Hexazinone residues in groundwater underlying plantation 83-8.

during sampling. The piezometric surface was observed to briefly decline from 0.2 m to 1.9 m in well VI when water was extracted from well IX. Thus, pumping of water from the deepest well resulted in the depression of water levels near the surface, indicating the potential for enhanced downward movement. The rate of natural vertical migration between sampling occasions is not known.

The highest hexazinone concentrations were observed in the deepest well (well IX). This implied that the peak concentrations of hexazinone were moving downward in a relatively narrow band. Detection of peak concentrations in wells VII and VIII may have been missed due to the downward movement either between the sampling intervals or during pumping prior to each sampling occasion. Hexazinone residues were reduced to less than the analytical limit of quantitation first in the most shallow wells (1096 days subsequent to treatment) followed by its disappearance in the deepest well 72 days later.

Hexazinone residues within the surficial aquifer underlying plantation site 86-1 were similar to those observed at plantation 83-8. Well installation at plantation 86-1 however occurred within approximately 60 days following hexazinone treatment. Concentrations of hexazinone initially observed in well VI (66 days after treatment) of 27.6 $\mu\text{g/L}$ increased to 46.2 $\mu\text{g/L}$, then declined to less than the analytical limit of quantitation after approximately 800 days (Figure 6). Although the surficial aquifer at plantation 86-1 was confined to the upper several meters compared to a much greater depth at plantation 83-8, the downward migration rate of hexazinone

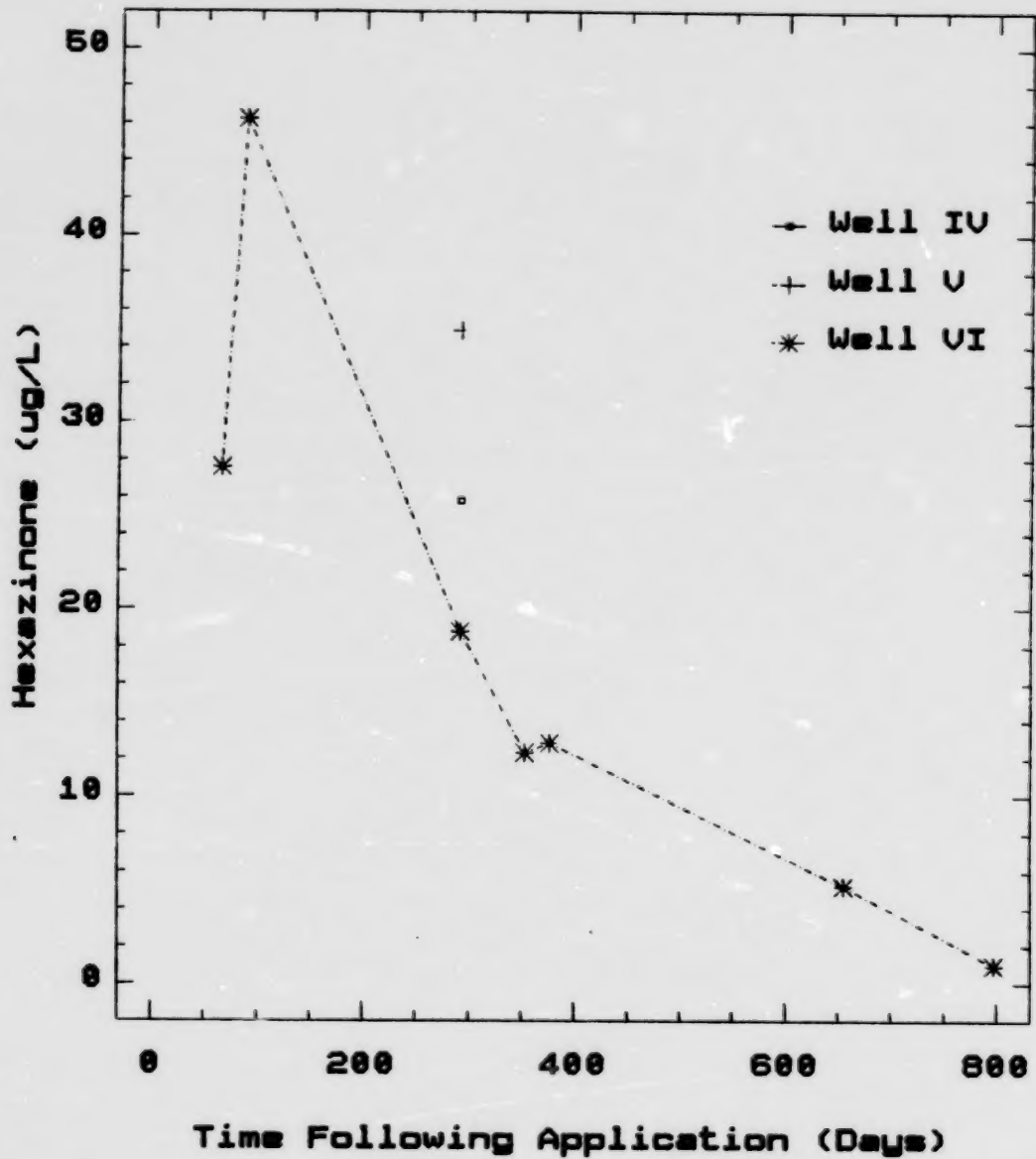


Figure 6: Hexazinone residues in groundwater underlying plantation 86-1.

monitored in the deepest respective wells was similar. That is, hexazinone residues were present immediately following well installation, increased to maximum concentrations near 50 $\mu\text{g/L}$, then declined to less than the analytical limit of quantitation during the subsequent 400 to 600 days. The piezometric water surface was usually below the screened intervals of wells IV and V, thus precluding the collection of groundwater samples from these wells.

The off-site movement of hexazinone within the surficial aquifer was monitored in wells I, II, and III at plantation 86-1. Wells I and II were located downgradient to the application site. Hexazinone residues were detected for a relatively short period of time in all wells, then declined to less than the analytical limit of quantitation (Figure 7). The highest concentration of 20.5 $\mu\text{g/L}$ was observed in well III. Concentrations in wells I and II did not exceed 10 $\mu\text{g/L}$. Higher concentrations of hexazinone within well III likely resulted due to its proximity to treated soils. Although the data indicated that lateral off-site migration of hexazinone can occur within the surficial aquifer, such movement within the study area was not significant as evidenced by the relatively low concentrations and the brief period of time during which hexazinone was detected.

The movement of organic compounds with infiltrating groundwater has been studied elsewhere. Roberts et al. (1982) followed the movement of organic compounds in reclaimed wastewater subsequent to groundwater injection. The movement of several compounds was examined and it was found that retardation occurred to different degrees. Retention times of the various organics were in

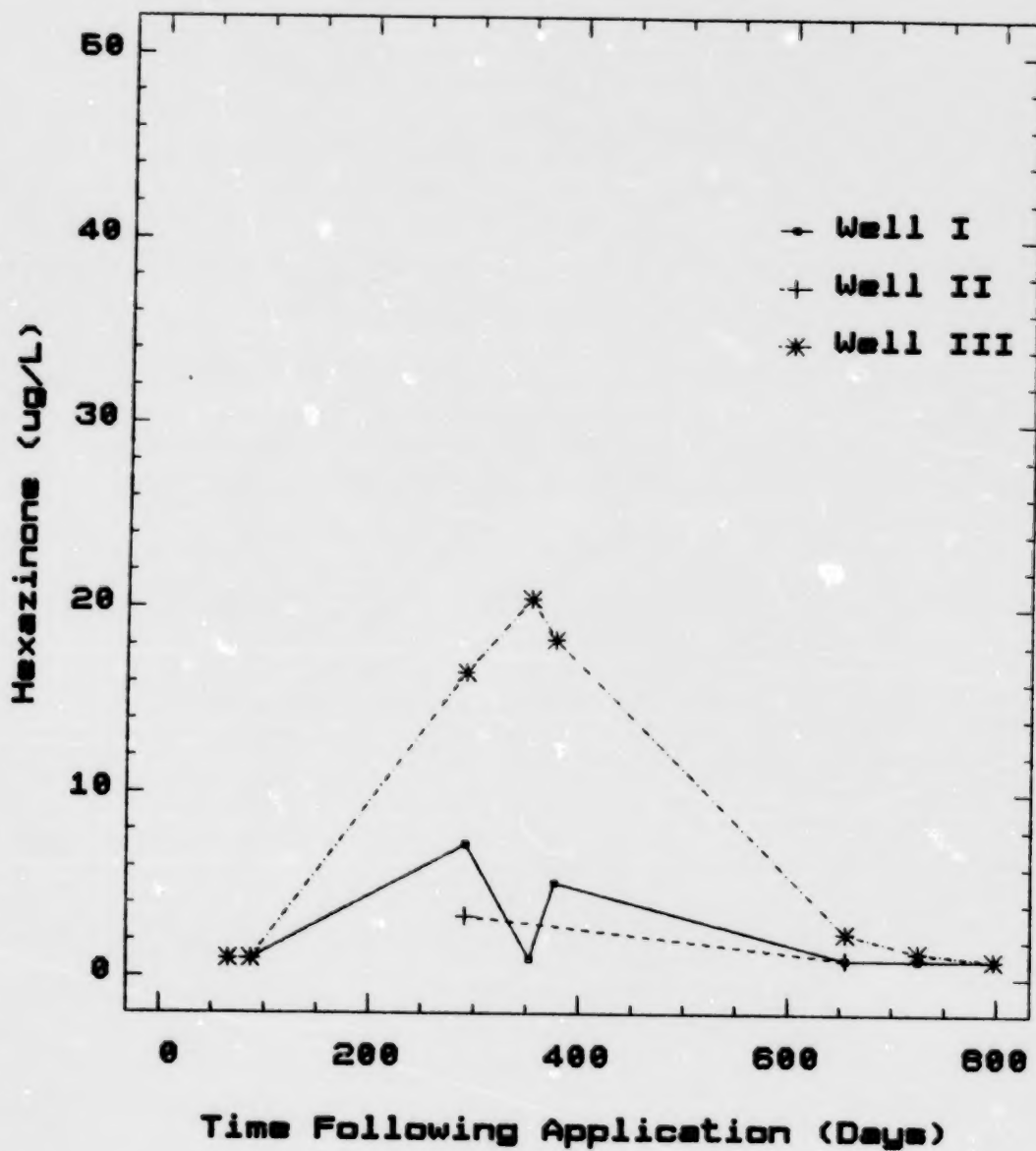


Figure 7: Hexazinone residues in groundwater adjacent to plantation 86-1.

approximate accord with their order of elution in gas chromatography. Retardation within the aquifer was attributable to sorption on aquifer substrate. Retardation was related to the hydrophobic nature of the organics. Roberts and Valocchi (1981) reported that movement retardation and concentration attenuation of organic compounds during groundwater infiltration can be predicted given knowledge of the organic content of the aquifer and the octanol-water partition coefficient* of the solute. The degree of attenuation is also dependent upon other aquifer characteristics such as distance travelled and the hydrogeological characteristics of the aquifer. Compounds of low octanol-water partition coefficients moving in aquifers of low organic carbon content are expected to move relatively freely. Schwarzenbach et al. (1983) observed similar results in field studies conducted in Switzerland. It was determined that organic compounds with octanol-water partition coefficients less than 5000 moved freely with infiltrating river water. Hence, the field results of Schwarzenbach et al. (1983) agreed well with original theoretical predictions.

* The octanol-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of a substance in the octanol phase to its concentration in 0.01 M $CaCl_2$. It is a measure of the degree of hydrophobicity of a substance. A substance with a large K_{ow} will partition in the organic solvent and is termed hydrophobic. A substance with a low K_{ow} will partition in the water phase and is termed hydrophilic.

Bouchard and Lavy (1985) reported the octanol-water partition coefficient for hexazinone to range from 9.26 to 11.86. This low K_{ow} for hexazinone was partially predicted by its relatively large solubility in water (3.3%). Bouchard and Lavy (1985) conducted adsorption-desorption studies with hexazinone on soil and on other organic substrates. It was determined that hexazinone was only weakly adsorbed by soil colloids.

Few field studies specific to hexazinone have been conducted. Neary et al. (1981) reported that 0.05% of hexazinone applied in the upper Piedmont region of Georgia was lost to subsurface water movement during an 8 month study period. Feng (1987) suggested that groundwater contamination following hexazinone application would not occur in areas containing silt loam soils with 5 to 10 cm of surface organic cover.

This study has shown that hexazinone has migrated with infiltrating groundwater to a depth of 13.8 m within an unprotected sand and gravel surface aquifer and has persisted within this environment for over 1000 days following application. This evidence is significant regardless that the movement may have been partially induced by the withdrawal of groundwater. The placement of piezometer test wells and the subsequent removal of water is implicitly an intrusive test procedure. Movement of groundwater therefore occurs at a rate that is enhanced from the natural state and which is related to the location of the well, the rate of water withdrawal and the hydrogeological features of the aquifer. Such conditions are similar, for example, to the extraction of groundwater from surficial aquifers for domestic use.

3.3 Aquatic Toxicology

Limited data exists on the toxicity of hexazinone to aquatic species. Johnson and Finley (1980) reported the 96 hr LC_{50} of Velpar towards both rainbow trout and bluegill to be greater than 100 mg/L. Dupont (1984) reported similar 96 hr LC_{50} values for rainbow trout and bluegill, ranging from 320 mg/L to 420 mg/L and from 370 mg/L to 420 mg/L, respectively. Further, Dupont (1984) reported the acute toxicity (96 hr LC_{50}) of Velpar L for the fathead minnow at 274 mg/L. Velpar was toxic to the aquatic crustacean Daphnia magna at a concentration of 151 mg/L in a 48 hr LC_{50} (Ibid).

Fowler (1977) reported that the aquatic macrophytes Myriophyllum verticillatum and Potamogeton pectinatus could be controlled with 1.0 mg/L hexazinone. Further, Fowler (1977) reported that the filamentous algae Vaucheria dichotoma, Rhizoclonium hieroglyphicum and Cladophora glomerata could be controlled with 0.5 mg/L hexazinone.

Velpar L inhibited reproduction of the green alga Selenastrum capricornutum Printz by 50% in an 18 day EC_{50} bioassay (Figure 8) at a concentration of 22.5 μ g/L. The 95% confidence limits ranged from 15.91 μ g/L to 31.50 μ g/L. A similar EC_{50} for this species was observed in the 4 day microtest. Reproduction was inhibited by 50% at a Velpar L concentration of 24 μ g/L (S.D = 3 μ g/L; n = 5) (Blaise pers. com.). The mode of action was apparently through blockage of photosynthetic processes (Ghassemi et al. 1982).

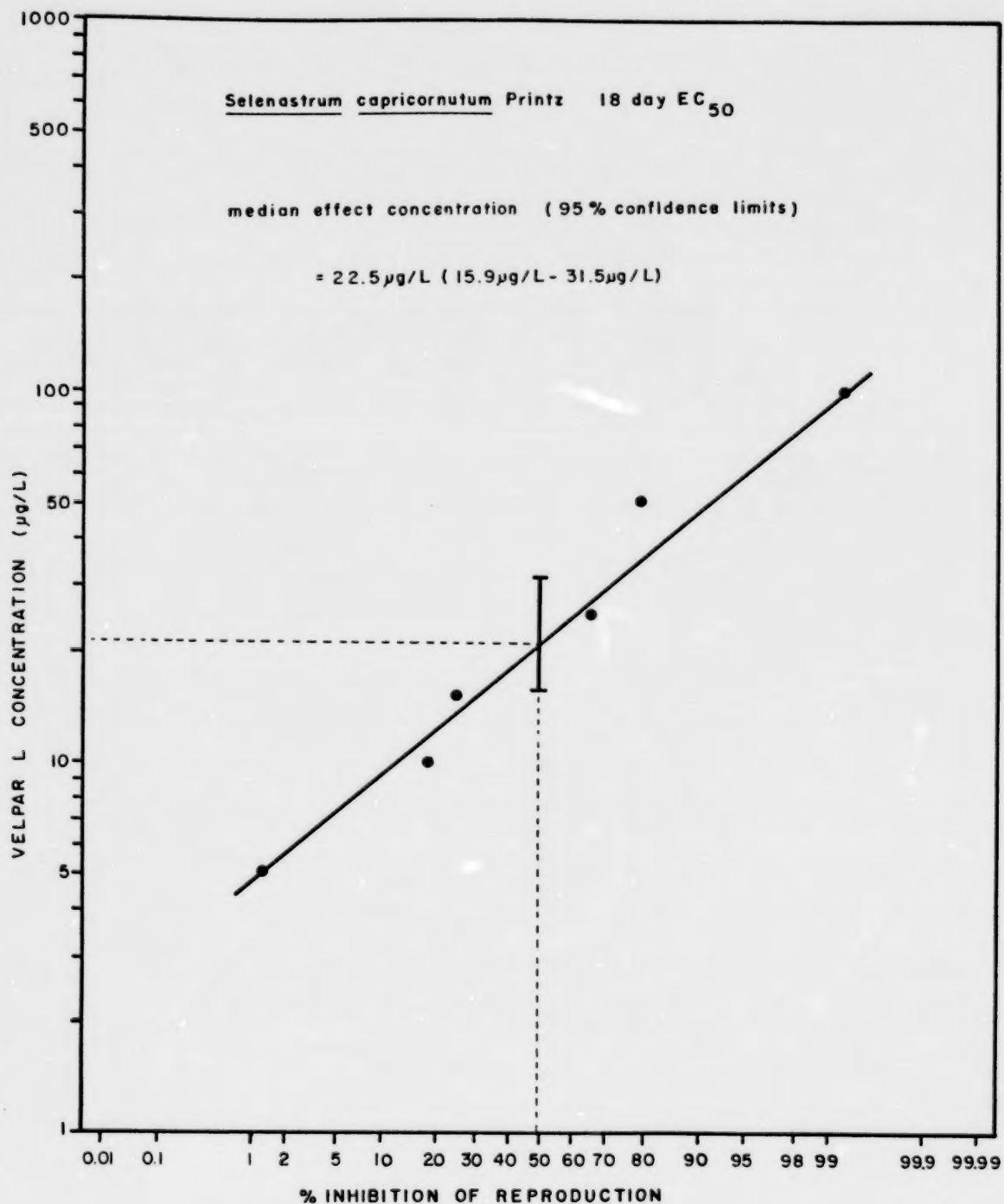


Figure 8: Graphical display of the *Selenastrum capricornutum* Printz 18 day EC_{50} bioassay results.

Mayack et al. (1982) did not observe major alterations of benthic invertebrate community structure or individual abundance in streams draining Velpar treated watersheds in Georgia. Hexazinone runoff, however, was relatively low. The aquatic invertebrate community was exposed intermittently to hexazinone concentrations ranging from 6 µg/L to 44 µg/L. In the study of Mayack et al. (1982) hexazinone residues were detected primarily during storm water runoff events and the residue peaks were short in duration. Assuming that the benthic invertebrates were similar in tolerance to hexazinone as the crustacean D. magna, the observed hexazinone concentrations would not have been expected to produce acute responses.

Fifty percent light inhibition was observed in Photobacterium phosphoreum in 5 minute and 15 minute Microtox bioassays at Velpar L concentrations of 1000 mg/L (S.D. = 340; n = 3) and 890 mg/L (S.D. = 352; n = 3) respectively (Blaise pers. com.). Hexazinone would not likely occur at such high concentrations in aquatic systems.

It would appear that the phytoplankton community is more sensitive to hexazinone contamination than other aquatic organisms. It is apparent that the major aquatic impact would manifest itself through the reduction of primary productivity. Secondary effects on aquatic receptors occupying other ecological compartments may be evidenced, depending upon the extent and duration of Velpar L persistence.

Toft (pers. com.) reported that an acceptable daily intake of hexazinone for humans had not been determined by Health and Welfare Canada, World Health Organization, United States National Academy of Sciences or United States Environmental Protection Agency. Although mammalian studies are weak, it is however reported that acute toxicity is low and that hexazinone is rapidly eliminated from the body (Ibid.). Accumulation within body tissues was not observed. Hexazinone was found not to be tumorigenic, mutagenic, teratogenic or to cause reproduction effects at sub-acute concentrations (Ibid).

Genotoxicity assessments using the S.O.S. chromotest indicated that Velpar L. did not invoke S.O.S. inducing potency activity above background when tested over a wide range of concentrations (Blaise pers. com.). Chromotest concentrations ranged from 7.5 to 951 nmoles without the metabolic activation microsomal fraction S9 and from 19 to 2378 nmoles with S9. Following DNA damage by chemical agents, E. coli has been shown to respond by invoking a set of functions entitled S.O.S. responses. The induction of such responses is closely correlated with the mutagenic properties of the chemical agent (Quillardet et al. 1982). These results thus confirm previous findings that Velpar L (including hexazinone) is not mutagenic.

Based upon 2-year feeding/oncogenicity studies with laboratory rats, a no observed effect level (NOEL) of 10 mg hexazinone/kg body weight was determined (Toft, pers. com.). Applying a safety factor of 100 and assuming that a 70 kg person would ingest 2 L of water per day, and assuming that water would be the only exposure source of hexazinone, a tentative calculated maximum acceptable criteria for hexazinone in drinking water would be 3.50 mg/L. The above assumptions are compatible with those described in Health and Welfare Canada (1978) and used to derive maximum acceptable criteria in drinking water for other organic substances.

The maximum observed concentration of hexazinone in subsurface groundwater is <2.0% of this tentative calculated maximum acceptable drinking water criteria derived for the protection of human health.

4.0 Conclusions

It was concluded that:

- 1) Some lateral movement of hexazinone from the treated plantations was evident in groundwater within the surficial aquifer. This movement however, occurred for a relatively brief period of time with hexazinone concentrations being less than 10 µg/L within 5 m of treated soils.
- 2) Vertical migration of hexazinone was observed within the surficial aquifer underlying the treated study plantations. Hexazinone was detected at maximum concentrations of 48.0 µg/L at a depth of 13.8 m.
- 3) Hexazinone residues persisted within the surficial aquifer for a period of approximately 1000 days following application.
- 4) Peak hexazinone concentrations appeared to move in a relatively narrow band within the surficial aquifer at a rate that was artificially enhanced due to the effect of groundwater sample extraction.
- 5) Hexazinone was detected in small surface water and surficial groundwater pools situated on treated soils for a period of approximately 1000 days following application.
- 6) A 50% reduction in reproduction was observed in an algal culture at a hexazinone median concentration of 22.5 µg/L. The most sensitive aquatic community receptor appeared to be phytoplankton.
- 7) Fifty percent light inhibition was observed with Photobacterium phosphoreum at approximate Velpar L concentrations of 1000 mg/L.

- 8) Velpar L was not mutagenic as evidenced by the S.O.S. chromotest.
- 9) The observed hexazinone concentrations in groundwater were less than 2% of the calculated tentative maximum acceptable drinking water criteria derived for the protection of human health.

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